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Molecular Design and Device Application of Radical **Polymers for Improved Charge Extraction in Organic Photovoltaic Cells**

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Final Report

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14. ABSTRACT
Radical polymers (i.e., macromolecules composed of non-conjugated backbone architectures and with stable radical sites present on the pendant groups of these backbones) are emerging as promising materials for organic electronic applications. While these materials have been used in a limited number of electrolyte-supported energy conversion and storage applications, the work presented within summarizes the first systematic findings of structure-property-performance relationships with respect to the solid-state electrical conductivity of radical polymers. In particular, we established the ready, scalable, and controlled synthesis of open-shell macromolecular homopolymers and block polymers. Furthermore, the solid-state electrical conductivity of a model radical polymer was determined to on the same order of magnitude as common pristine (i.e., not doped) conjugated polymers. Therefore, these radical polymers have proven to be: (1) synthetically-simple, (2) environmentally-robust, and (3) relatively high-performing with respect to many oft-used conjugated polymers. As such, this program has advanced the state-of-the-art with respect to novel polymer electronics and promoted the career of an early-stage investigator with a research portfolio centered on the needs of the DoD.

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AFOSR YIP: Final Performance Report
Grant #FA9550-12-1-0243
May 1, 2012 (Start of Period of Performance) – April 30, 2015

Lead Organization: Purdue University
Technical Point of Contact: Professor Bryan W. Boudouris
Administrator Point of Contact: Ms. Helen Moschinger

Proposal Title

AFOSR YIP (2012): Molecular Design and Device Application of Radical Polymers for Improved Charge Extraction in Organic Photovoltaic Cells

AFOSR Program Manager: Dr. Charles Lee

Unabridged Abstract

Radical polymers (*i.e.*, macromolecules composed of non-conjugated backbone architectures and with stable radical sites present on the pendant groups of these backbones) are emerging as promising materials for organic electronic applications. While these materials have been used in a limited number of electrolyte-supported energy conversion and storage applications, the work presented within summarizes the first systematic findings of structure-property-performance relationships with respect to the solid-state electrical conductivity of radical polymers. In particular, we established the ready, scalable, and controlled synthesis of open-shell macromolecular homopolymers and block polymers. Furthermore, the solid-state electrical conductivity of a model radical polymer was determined to be of ~10^{-5} S cm^{-1}. This is on the same order of magnitude as common pristine (*i.e.*, not doped) π-conjugated polymers, which highlights the great promise of these next-generation materials. Additionally, the environmental stability (*i.e.*, resistance to oxygen and humidity) and voltage-dependence of radical polymer thin films was found to be quite robust; this was despite the lone electron nature of the radical site. Therefore, these radical polymers have proven to be: (1) synthetically-simple, (2) environmentally-robust, and (3) relatively high-performing with respect to many oft-used conjugated polymers. Because of these advantageous properties, radical polymer thin films have been included in a number of advanced organic electronic devices. Thus, through the support of the AFOSR and the Young Investigator Program, we have been able to establish these macromolecules as exciting alternatives to traditional polymer conductors. Moreover, this effort has established our laboratory as a world leader in the polymer synthesis, polymer physics, and solid-state device application of these unique macromolecules. As such, this program has advanced the state-of-the-art with respect to novel polymer electronics and promoted the career of an early-stage investigator with a research portfolio centered on the needs of the Department of Defense.

Executive Summary of Research Accomplishments and Technical Achievements

During the three years of the Young Investigator Program (YIP) work regarding radical polymers, we have been the first in the world to establish these materials as solid-state conductors, and we have demonstrated that these materials are extremely promising candidates as flexible, transparent electrodes. Additionally, we have demonstrated the synthetic flexibility associated with these macromolecules by generating block polymers with other non-conjugated repeat units. Furthermore, we have shown the relative robustness of these materials with respect to bias stressing and environmental conditions. As such, these three years of work have set the stage for radical polymers, and have served as the cornerstone for their emergence in the organic electronics device community. This would not have been possible without the AFOSR support, and we greatly thank the agency for this opportunity to improve energy conversion devices for the warfighter and to advance the scientific knowledge of the United States. In particular, we thank the YIP as it provided the very necessary funding, with limited preliminary results, such that we could make these significant impacts. It is highly unlikely that this work would have been funded through more traditional means, given the early-stage nature of the Principal Investigator's (PI's) independent career when the project began. Therefore, we are especially thankful for this program and for the excellent guidance provided by the program manager, Dr. Charles Lee. In this final report, we detail the specific accomplishments of the previous 3 years. In an abbreviated form, these major technical objectives can be summarized as follows. We have:

1. Synthesized radical polymers using two controlled radical polymerization mechanisms: (1) atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. Both of these polymerization mechanisms have led to materials with readily-controlled molecular weights and narrow molecular weight distributions. Additionally, we were able to use these techniques to synthesize polymers in large (> 10 g) batches at the laboratory scale and without residual metal impurities present in the samples.
2. Established that radical polymers are capable of conducting charge at the same rate as common π-conjugated polymers that are not doped with any chemical agents [*e.g.*, poly(styrene sulfonate) (PSS)]. Furthermore, this conductivity was found to be isotropic in nature. This lack of directional preference in the charge transport is ascribed to the fact that radical polymers are glassy in the solid state. As such, there is no preferred direction due to crystal structure or crystal texture of the materials. This is a distinct difference from what is observed commonly in semicrystalline polymer conductors.
3. Verified that the conducting radical polymers are remarkably transparent in the visible region of the electromagnetic spectrum. That is, these materials are ~100-fold more transparent than the commonly-used transparent conducting polymer poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS). This is to be expected due to the lack of conjugation in the radical polymer macromolecular backbone.
4. Doped the radical polymers with small molecule radical analogs in order to increase the conductivity of the materials. This increase in conductivity occurred due to a higher density of radical sites that could undergo the oxidation-reduction (redox) reaction. This higher density of sites decreased the distance between adjacent radical groups, which

increased the likelihood of an exchange event. Unfortunately, a maximum in conductivity was established as a function of small molecule loading because higher loadings of the small molecule additive caused poor film formation for the radical polymer-based materials.

5. Measured the hole mobility of a pristine radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) and found it to be ~10^{-4} cm^2 V^{-1} s^{-1}. Again, this is on par with the space charge-limited mobility of many common conjugated polymers. As such, this effort reaffirmed the idea that charge transport in radical polymers could be tuned to be at a rate that is equal to (or greater than) even the most-advanced conjugated polymer systems.
6. Shown that the mobility of charges in radical polymers is temperature-independent if the radical polymer thin film is in the glassy state. This observation is in direct agreement with the idea that radical-radical interaction (*i.e.*, not the rate of the charge transfer reaction) is the limiting step in radical polymer-based charge transport. As such, this effort demonstrated the promise of using radical polymers with glass transition temperatures near or below room temperature. This line of thinking continues to be an active field of research within our group.
7. Identified the chemical nature of radical polymers using complementary techniques that demonstrate that the bulk behavior of the radical polymers is similar to that of the thin film nature. That is, there is no apparent change in chemical structure or electronic properties when the materials are cast from solution into the solid state.
8. Established that the exact chemical identity of the pendant groups associated with the radical polymer can impact charge transport by an order of magnitude. This detailed study proved that the conditions used to oxidize the protected polymer precursor to the radical polymer can lead to materials with vastly different charge transport properties. This particular work has been of immense interest to other research groups who are beginning to utilize radical polymers in myriad applications.
9. Quantified the behavior of radical polymers as a function of radical density. This was accomplished through a combination of detailed synthetic experiments and electron paramagnetic (EPR) spectroscopy measurements. Importantly, this allowed us to consistently quantify the radical density in our materials in a relatively straightforward manner in all future experiments.
10. Produced a review paper that highlights the history of radical polymers and offered a perspective of their potential organic electronic applications moving forward. This work cemented our group as a world leader in the study of radical polymers.
11. Synthesized radical polymer-containing diblock copolymers. Additionally, we showed how the assembly of the block polymer thin films could be directed using simple solvent annealing techniques. In this way, we were able to form continuous, nanostructured domains based on radical polymers. This is a very difficult objective to achieve using conjugated block polymer species.
12. Demonstrated that the radical polymer thin films retain their relatively high conductivity values after exposure to oxygen, water vapor, and solar illumination. In particular, the

materials are remarkably stable over the course of multiple hours and up to, at least, days of exposure to common environmental stresses.

13. Stressed the radical polymer thin films with respect to extreme voltage biasing conditions and times. We verified that the radical polymer thin films do not show a change in performance over the course of this bias stressing and that no breakdown of the materials was observed. Again, this highlights the potential for radical polymers to be implemented in long-term missions were device flexibility and transparency are of import.
14. Introduced radical polymer thin films to environments with different levels of moisture in the atmosphere. Once removed from the humid environment, the electrical performance of the radical polymers returns to the value it was prior to the exposure. This demonstrates that radical polymers are immune to being exposed to varying levels of humidity.
15. Doped radical polymer thin films with small molecule cationic analogs of the radical pendant group moiety (*i.e.*, nitroxide radicals) in order to increase the conductivity of the radical polymer-based thin films. We have established that this increase in conductivity occurs both due to electrochemical means and due to better film formation caused by the addition of the plasticizing dopants.

Accomplishing the above objectives has resulted in tangible metrics for this project in terms of education of students, dissemination of results, national recognition for our work, and funding for new projects. In particular, the support through the AFOSR YIP award has allowed the following events to occur over the past year.

1. Two doctoral students have worked on this project during the duration. One of the students (Baradwaj) was funded through the AFOSR YIP award, and the other student (Rostro) was funded through the National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP). Rostro defended her doctoral thesis in July of 2015 and Baradwaj is scheduled to defend his doctoral thesis in May of 2016. Three undergraduate students significantly contributed to this project as well. One of these students will be returning senior at Purdue next year. Another student will be attending medical school in the upcoming year. The third student will continue his chemical engineering studies by attending the chemical engineering graduate program at the University of Minnesota. Additionally, one high school student has worked significantly on this project, and this student is planning on majoring in an engineering discipline when he begins his university career.
2. Seven manuscripts have been published to date due to work supported by the AFOSR YIP award. Furthermore, 1 manuscript is currently in press, 2 manuscripts are under review currently, and 1 manuscript is in preparation. Therefore, we anticipate having, at least, a final total of 11 manuscripts published due to the support of the AFOSR YIP award (see below for exact referencing). We note that all publications have recognized the support of the AFOSR in the Acknowledgements sections of the manuscripts.

   The seven published manuscripts are the following.

a. “Engineering Optoelectronically-active Macromolecules for Polymer-based Photovoltaic and Thermoelectric Devices,” Boudouris, B. W. *Current Opinion in Chemical Engineering* **2013**, *2*, 294-301.

b. “Controlled Radical Polymerization and Quantification of Solid State Electrical Conductivities of Macromolecules Bearing Pendant Stable Radical Groups,” Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. *ACS Applied Materials and Interfaces* **2013**, *5*, 9896-9901.

c. “Quantification of Solid-State Charge Mobility in a Model Radical Polymer,” Baradwaj, A. G.; Rostro, L.; Alam, M. A.; Boudouris, B. W. *Applied Physics Letters* **2014**, *104*, 213306.

d. “Solid State Electrical Conductivity of Radical Polymers as a Function of Pendant Group Oxidation State,” Rostro, L.; Wong, S. H.; Boudouris, B. W. *Macromolecules* **2014**, *47*, 3713-3719.

e. “Defect Characterization in Organic Semiconductors: Forward Bias Capacitance Analysis,” Ray, B.; Baradwaj, A. G.; Boudouris, B. W.; Alam, M. A. *Journal of Physical Chemistry C* **2014**, *118*, 17461–17466.

f. “Radical-containing Polymers and Their Applications to Organic Electronic Devices,” Tomlinson, E. P.; Hay, M. E.; Boudouris, B. W. *Macromolecules* **2014**, *47*, 6145–6158.

g. “Synthesis and Thin Film Self-Assembly of Radical-Containing Diblock Copolymers,” Rostro, L.; Baradwaj, A. G.; Muller, A. R.; Laster, J. L.; Boudouris, B. W. *MRS Communications* **2015**, *available online*.

The one manuscript that has been accepted is the following.

h. “Collection-limited Theory Interprets the Extra-ordinary Response of Single Semiconductor Organic Solar Cells,” Ray, B.; Baradwaj, A. G.; Khan, M. R.; Boudouris, B. W.; Alam, M. A. *Proceedings of the National Academy of Science* **2015**, *accepted*.

The two manuscripts that are under review are the following.

i. “Design of Super-Paramagnetic Core-Shell Nanoparticles for Enhanced Performance of Inverted Polymer Solar Cells,” Jaramillo, J.; Barrero, C.; Boudouris, B. W.; Jaramillo, F. **2015**, *submitted for review*.

j. “On the Environmental and Electrical Bias Stability of Solid-State Radical Polymer Conductors,” Baradwaj, A. G.; Rostro, L.; Boudouris, B. W. **2015**, *submitted for review*.

The one manuscript that is in preparation is the following.

k. “Enhanced Electrical Conductivity in Radical Polymers through Systematic Doping with Small Molecule Salts,” Baradwaj, A. G.; Jochem, K. S.; Boudouris, B. W. **2015**, *in preparation*.

3. Support from the AFOSR YIP program also has allowed our work to be presented, through invited and contributed talks and poster sessions, across the nation. We note that

all presentations have recognized the support of the AFOSR. The following presentations were delivered during the 3-year period of funding. **Bolded** text indicates a student was the presenter.

a. *Invited Presentation. Poster Presentation. “Radical Polymers for Nanostructured, Next Generation Thermoelectric Devices.” DARPA Young Faculty Award Kick-Off Meeting. July 2012.

b. *Invited Presentation. Oral Presentation. “Design of Optoelectronically-active Polymers for Organic Photovoltaic Applications.” Purdue Solar Research Series, Birck Nanotechnology Center. January 2013.

c. Contributed Presentation. Oral presentation. “Aliphatic Polymers Bearing Pendant Radical Groups as Charge Carrying Moieties in Organic Electronic Applications.” APS March Meeting, Baltimore, MD. March 2013.

d. Contributed Presentation. **Poster Presentation. Lizbeth Rostro and Bryan W. Boudouris.** “Solid State Charge Transport in Radical Polymers.” APS March Meeting, Baltimore, MD. March 2013.

e. *Invited Presentation. Oral Presentation. “Designing Macromolecules with Specific Optoelectronic and Chemical Functionalities for Advanced Energy and Biomedical Applications.” Purdue University, Department of Chemistry (Organic Chemistry Division). April 2013.

f. Contributed Presentation. **Poster Presentation. Biswajit Ray, Aditya G. Baradwaj, Bryan W. Boudouris, and Muhammad A. Alam.** “Capacitance Collapse in Forward Bias Fingerprints Defects in Organic Semiconductors.” MRS Spring Meeting, San Francisco, CA. April 2013.

g. *Invited Presentation. Oral Presentation. “The Utilization of Radical Polymers in Next-Generation Organic Electronic Devices.” United States Air Force Academy. October 2013.

h. Contributed Presentation. Oral Presentation. “Optimizing Solid State Conductivity in Radical Polymer.” AIChE Annual Meeting, San Francisco, CA. November 2013.

i. Contributed Presentation. **Poster Presentation. Aditya G. Baradwaj, Lizbeth Rostro, and Bryan W. Boudouris.** “Quantifying the Solid State Charge Transport Characteristics of Radical Polymers.” APS March Meeting, Denver, CO. March 2014.

j. Contributed Presentation. **Oral Presentation. Lizbeth Rostro, Aditya G. Baradwaj, and Bryan W. Boudouris.** “Synthesis and Solid State Charge Transport in Radical Polymers.” APS March Meeting, Denver, CO. March 2014.

k. *Invited Presentation. Oral Presentation. “Non-conjugated Radical Polymers as an Emerging Class of Transparent Conductors in Organic Photovoltaic and Thermoelectric Applications.” 30th International Conference of the Polymer Processing Society, Cleveland, OH. June 2014.

l. *Invited Presentation. Oral Presentation. “Designing Macromolecules with Specific Optoelectronic and Chemical Functionalities for Advanced Membrane and Energy Conversion Applications.” Purdue University, School of Chemical Engineering. September 2014.

m. Contributed Presentation. Oral presentation. Bryan W. Boudouris, Lizbeth Rostro, Aditya G. Baradwaj, and Martha E. Hay. “Correlating Transport with Nanostructure and Chemical Identity in Radical Polymer Conducting Glasses.” APS March Meeting, San Antonio, TX. March 2015.

n. **Oral presentation. Lizbeth Rostro, Si Hui Wong, Lucio Galicia, and Bryan W. Boudouris.** “Design of Radical Polymers as Transparent Conductors in Organic Photovoltaic Devices.” APS March Meeting, San Antonio, TX. March 2015.

o. *Invited Presentation. Oral Presentation. “Designing Macromolecules for Advanced Energy Conversion and Nanofiltration Applications.” University of Minnesota, Department of Chemical Engineering and Materials Science. April 2015.

p. *Invited Presentation. Oral Presentation. “Designing Macromolecules for Advanced Energy Conversion and Nanofiltration Applications.” University of Wisconsin – Madison, Department of Chemistry. May 2015.

q. *Invited Presentation. Oral Presentation. “Radical Polymers in Solid-State Organic Electronic Devices.” American Chemical Society (ACS) Fall 2015 Meeting, Boston, MA. August 2015.

r. *Invited Presentation. Oral Presentation. “Charge Transport Physics of Non-conjugated, Glassy Radical Polymer Conductors.” Institute of Physics - Polymer Physics Group 2015 Meeting, Manchester, United Kingdom. September 2015.

s. *Invited Presentation. Oral Presentation. “Designing Radical Polymers for Solid-State Organic Electronic Applications.” University of Illinois at Urbana-Champaign, Department of Chemical and Biomolecular Engineering. October 2015.

t. *Invited Presentation. Oral Presentation. “The Redox-Active Behavior of Radical Polymers.” Electrochemical Society (ECS) Fall 2015 Meeting, Phoenix, AZ. October 2015.

u. *Invited Presentation. Oral Presentation. “Tuning the Thin Film Self-Assembly of Radical-Containing Diblock Copolymers.” American Institute of Chemical Engineers (AIChE) Fall 2015 Meeting, Salt Lake City, UT. November 2015.

v. *Invited Presentation. Oral Presentation. “Designing Radical Polymers for Solid-State Organic Electronic Applications.” Massachusetts Institute of Technology, Program in Polymers and Soft Matter. November 2015.

4. The results acquired through the AFOSR YIP program have allowed us to be recognized with a number of other awards during the 3 years of YIP funding. These awards have had both a domestic and international flavor. Specifically, these awards include the following.

a. The Defense Advanced Research Projects Agency (DARPA) Young Faculty Award (YFA) – 2012
b. Invited Participant to the National Academy of Engineering's (NAE's) Frontiers of Engineering (FOE) – 2013
c. American Physical Society (APS) Division of Polymer Physics – UK Polymer Physics Group (PPG) Lectureship – 2015

By being the first in the world to decipher the fundamental properties of an emerging class of electronically-active polymers, radical polymers, we have been able to address a number of points regarding their utilization in organic electronic devices. These promising materials can be used in a number of practical applications currently. Furthermore, we anticipate that their utilization will expand as we continue our work regarding the molecular structure-charge transport property-device performance relationships of radical polymers in the future. This AFOSR YIP opportunity was the ideal launching point for this exciting line of work that will truly last an entire career. None of these successful works would have been possible without the financial support from the AFOSR and mentoring support from our program manager, Dr. Charles Lee. Therefore, we thank both parties greatly.

Detailed Research Results and Future Technical Objectives

Introduction

Polymers with optoelectronic functionality have been of increasing interest due to the capability of these soft materials to complement their inorganic counterparts in applications where flexible, mechanically-robust devices are desired. Furthermore, the ability to impart tailored functionalities to these polymers, by synthetically altering their chemical constituents, affords researchers the opportunity to refine macromolecular architectures for optimized performance. Previously, the majority of the effort regarding these promising macromolecules has focused on polymers with a closed-shell electronic valence structure, and with a high degree of π-conjugation along the polymer backbone (*i.e.,* π-conjugated polymers). This focus has been with good merit, as the highest-performing polymers for organic electronic applications have been those with large degrees of conjugation along their backbones, and the underlying physical phenomena that allow for these materials to perform well has been studied for a good period of time. In this way, the structure-property-performance relationships of these materials are becoming rather understood. However, electronically-active polymers are not limited to this one set of functional materials. Another design manifestation is that of non-conjugated oxidation-reduction-active (redox-active) polymers. While many types of redox-active polymers have played important roles in a variety of organic electronic applications, radical polymers are an emerging subclass of these redox-active polymers that are solely organic in nature. In the work for this award, the term radical polymer is defined as a macromolecule with a non-conjugated backbone and with stable radical groups that are pendant to this non-conjugated macromolecular backbone. Prior to the work presented here, radical polymers had been utilized almost exclusively in electrolyte-supported (*i.e.*, battery) applications. This excellent previous work established that there were tangible benefits to implementing radical polymers in energy storage devices; however, no work regarding the utilization of these materials in energy conversion devices had occurred. Furthermore, only very limited work had been performed in regards to

elucidating the underlying physics of solid-state charge transport in radical polymers. During this AFOSR YIP effort, our team was able to make significant advances upon both fronts, and this report (in addition to the publications listed above) summarizes the major findings of these efforts.

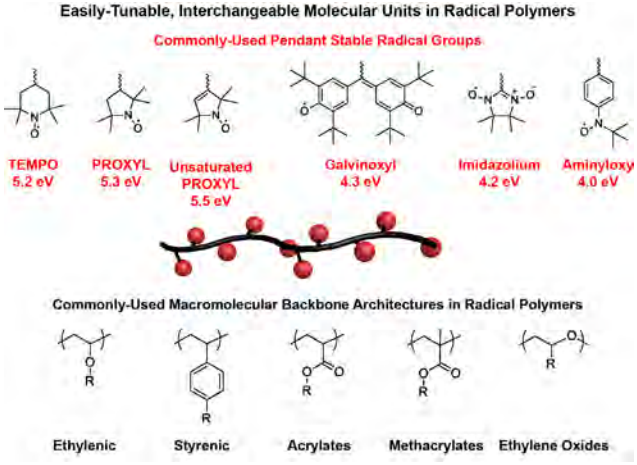

Figure 1. Commonly-used open-shell pendant group and macromolecular backbone chemical functionalities are depicted. The chemistry of the small molecule stable radical group dictates the SOMO energy level of the radical polymer and, thus, the preference of the radical polymer to be oxidized (left 3 radical chemistries) or reduced (right 3 radical chemistries). Note that the decoupled nature of the radical polymer backbone (black line) and the pendant radical groups (red spheres) allows for independent tuning of these two key moieties within the radical polymer.

Central to the electronic functionality of radical polymers are the stable pendant radical groups along the backbone of the polymer. In order to ensure that these species are long-lived, the unpaired electrons are stabilized in radical polymers by: (1) bulky substituent groups; (2) through the use of heteroatoms; or (3) through substituent groups that contain a substantial degree of conjugation in the pendant group (example chemical structures of common radical polymers are shown in Figure 1). Therefore, a key design parameter regarding the pendant groups of these radical polymers is one that dictates that they are reactive enough to undergo rapid charge transfer reactions for high-performance electronic functionality, but stable enough to withstand the relatively harsh conditions associated with device operation. In the initial work presented here, we have focused exclusively on a nitroxide (*i.e.*, the TEMPO moiety of Figure 1) radical chemistry. This focus was intentional as the TEMPO functional group has demonstrated long lifetimes in numerous applications and the synthetic chemistry associated with radical polymer based on the TEMPO-like group are readily-amenable to our polymerization protocols (*vide infra*). In the solid state, macroscopic charge transport occurs through a series of single electron charge transfer reactions between these stable pendant radical groups. That is, upon the creation of a high density of stable radical sites, the intramolecular and intermolecular charge transport occurs through a one-electron transfer of valence shell electrons that does not result in the breaking or formation of chemical bonds. For example, the nitroxide functionality can undergo an oxidation reaction to form the oxoammonium site or be reduced to form the aminoxyl anion. Due to the unstable nature of the radical and ionic sites, these electron exchange reactions between neighboring pendant groups occur in a rather facile manner, if the radical sites are in close enough proximity for the reaction to occur. This solid-state charge transport is thought to occur through an electric field-driven mechanism, in a manner akin to many disordered π-conjugated semiconductors that lack crystalline domains. Here, application of an external electric field promotes the injection of a charge onto the polymer chain from an electrode, and this charge subsequently is transported from neighboring radical site to neighboring radical site. Therefore, much of the work performed during this award examined

how the synthetic parameters associated with a model radical polymer could be used to enhance the electrical conductivity of the materials.

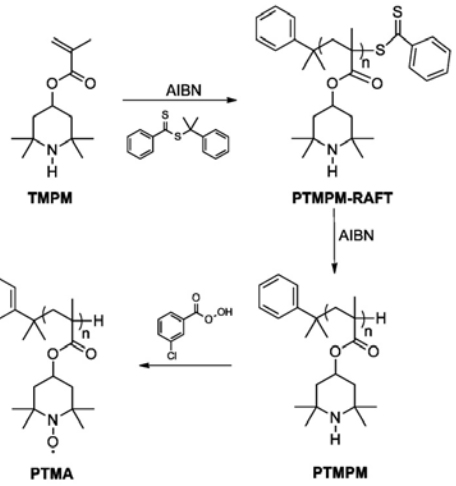

Figure 2. The synthetic route utilized to generate the radical polymer PTMA through a RAFT-mediated polymerization mechanism.

Results and Discussion

In our first effort, we developed a methodology to produce radical polymers with controlled molecular weights that does not require the use of metal catalysts, which can be difficult to remove from the final polymer product. As such, we were confident that the observed optoelectronic properties of the polymers were intrinsic in nature and not due to unintentional doping from reaction impurities. The synthetic methodology used for this reaction system is shown in Figure 2; here, the first step of the procedure involved the polymerization of the 2,2,6,6-tetramethyl-4-piperidinyl methacrylate (TMPM) monomer to generate poly(2,2,6,6-tetramethyl-4-piperidinyl methacrylate) (PTMPM-RAFT). Because a RAFT polymerization scheme was utilized, the molecular weights of the polymers could be tuned to a predetermined value in the range of 5 kg mol^{-1} and 24 kg mol^{-1}, as measured by size exclusion chromatography (SEC) against polystyrene (PS) standards. Furthermore, dispersity ($Đ$) values of the polymers were found to be 1.2, as measured against PS standards, highlighting the controlled nature of the polymerization. This controlled polymerization of a radical polymer through a RAFT-mediated route was the first of its kind in the literature.

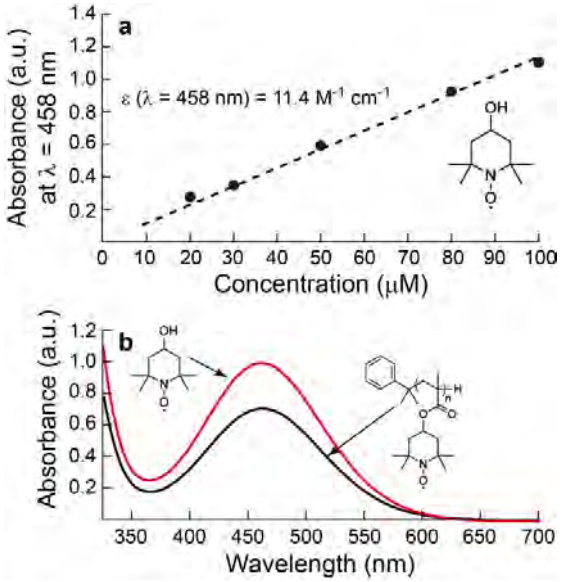

Figure 3. (a) Absorbance of the small molecule, TEMPO-OH (the chemical structure is inset in the figure), in chloroform, which is the small molecule analog to the pendant groups of PTMA. The measured molar absorptivity of this molecule was used to determine the concentration of pendant radicals in PTMA solutions. The dashed line is a linear regression fit to the data points. (b) UV-Vis absorbance spectra of PTMA (black curve) in chloroform at a concentration of 30 mg mL^{-1}. The red curve of (b) is the absorption spectrum of small molecule TEMPO-OH that would indicate 100% conversion of the protected pendant groups.

After confirmation of the removal of the chain transfer end group to form the PTMPM molecule, the conversion of PTMPM to PTMA was quantified by measuring the ultraviolet-visible light absorbance of the material pre- and

post-oxidation using the *meta*-chloroperbenzoic acid (*m*CPA) group shown in Figure 2. First, the molar absorptivity of the radical pendant group was determined utilizing the radical-bearing small molecule analog, (4-hydroxy-2,2,6,6-tetramethyl-piperidinyl)oxidanyl (TEMPO-OH), whose concentration could be controlled readily in solution. The molar absorptivity of this small molecule was found to be 11.4 M^{-1} cm^{-1} (Figure 3a) using a simple Beer's Law regression. By utilizing this value, the concentration of radicals present in PTMA-containing solutions could be calculated in a straightforward manner. This was done by dissolving a known amount of PTMA (with a known molecular weight) into a chloroform solution after oxidation of the PTMPM to PTMA. As shown in Figure 3b, the conversion of PTMPM to PTMA was not complete. In fact, the percent conversion of protected pendant groups to the radical groups was only 69 ± 4%. To our knowledge, this was the first quantitative report of the conversion of radical groups, and these data suggested that a better oxidizing agent or better oxidation conditions could prove extremely useful in generating PTMA molecules with complete radical conversion; this would increase charge transport ability of the functional polymers. In fact, in a follow-on piece to this original work, controlling and quantifying the radical density was determined to have a remarkably large effect on the charge transport ability of PTMA.

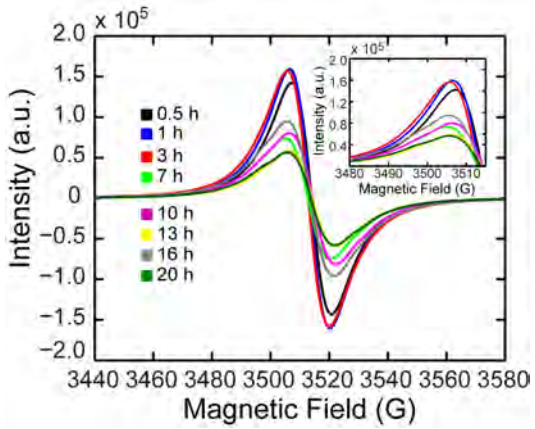

Figure 4. EPR spectra for PTMA as a function of oxidation time. The absorption intensity, corresponding to the radical density, initially increases as oxidation time increases up to 3 hours. After 3 hours the radical density decreases significantly and then stabilizes. The reduction in intensity of the free radical signal from EPR as a function of oxidation time demonstrates that the radical density is decreasing with oxidation time, suggesting the over-oxidation to a non-radical species. These data were acquired for a solution composed of 2 mg of PTMA in 1 mL of toluene.

That is, beyond a very recent and impressive anionic polymerization-based result that was able to synthesize PTMA with every pendant group containing a stable radical species, most synthetic protocols call for the creation of the polymer bearing protected pendant groups, PTMPM, followed by the oxidation to the stable radical species (PTMA), as shown in Figure 2. However, the effects of the oxidation reaction that creates the stable radicals on the pendant groups for this common procedure had not been elucidated fully until our second report on radical polymers. Specifically, we established the effects of the oxidation reaction on the solid-state electrical conductivity of PTMA. Again we used *meta*-chloroperbenzoic acid to oxidize PTMPM to form PTMA and demonstrated that, after forming the stable radical site, there can be further oxidation to form the cation analog ($PTMA^+$) and the hydroxylamine analog (PTMA-OH). The parent polymer, PTMPM, was synthesized as previously shown, via a RAFT-mediated polymerization scheme. From the same parent polymer, the oxidation reaction, using the same oxidation reagent solution, was performed in inert conditions at room temperature with an excess of *m*CPBA to produce the stable radical sites followed by a wash with an aqueous sodium carbonate solution. During this reaction and subsequent workup, the pendant groups in PTMA have demonstrated the ability to undergo a disproportionation reaction under acidic conditions to form the oxidized counterpart of PTMA (*i.e.,* +N=O) and the hydroxylamine

pendant group (*i.e.*, N-OH). Such a reaction resulted in the decreasing concentration of radicals in PTMA, which was monitored in solution directly via EPR (Figure 4). The signal intensity associated with the radical spin density decreased with longer oxidation reaction time, confirming that the radical population decreased as oxidation time increases. Similar behavior was observed for the small molecule radical analog, 4-hydroxy TEMPO (TEMPO-OH), which also exhibited a single peak in EPR at the same applied magnetic field. Moreover, the single peak in toluene for both TEMPO-OH and PTMA was indicative of the high concentration of radicals in solution. The radical density monitored via EPR suggested three oxidation stages, the first corresponded to shorter oxidation times (up to 1 h) where the pendant groups were being functionalized to the stable radical. After an hour, the radical density was constant until the three hour mark. At this point the pendant groups were being over-oxidized to the cationic species, $PTMA^{+}$, while continuing to form the stable radical from segments of the chain that were still protected (*i.e.*, PTMPM). Following this mild doping stage, the radical density fell significantly and remained roughly constant for oxidation times up to 20 hours. These results suggested that the oxidation reaction proceeds to form other species after forming the stabilized radical.

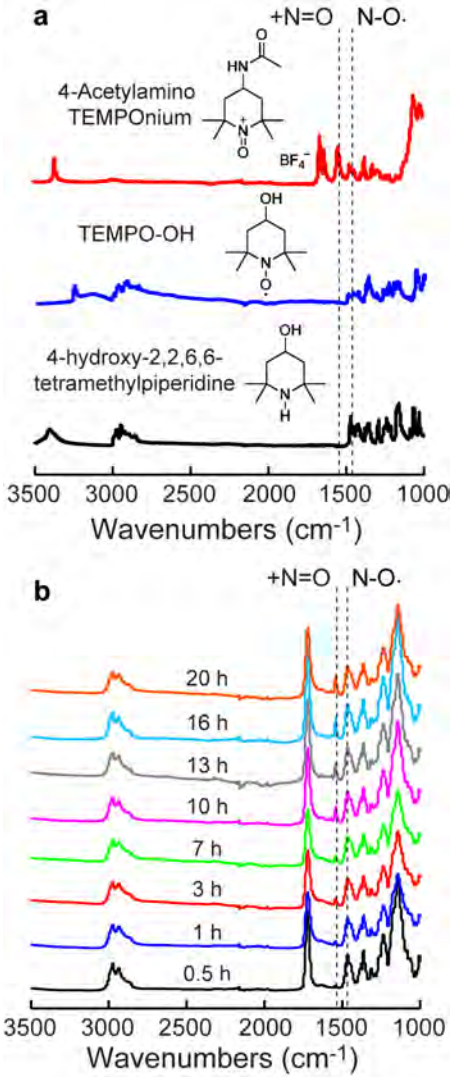

Figure 5. (a) ATR-FTIR spectra of the small molecule analogs of the possible pendant group functionalities in PTMA: N-H, N-O•, and +N=O. (b) ATR-FTIR spectra of PTMA as a function of oxidation time, demonstrating an increase in cations present with increasing oxidation reaction time. The peak at 1467 cm^{-1} is associated with N-O• while the peak at 1540 cm^{-1} is associated with +N=O. All peaks are normalized to the peak of at ~3000 cm^{-1}, associated with the alkyl C-H chemical functionality.

The conversion of the radical functionality to that of the cationic species can be observed to increase in the solid state as well. That is, attenuated total internal reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy and x-ray photoemission spectroscopy (XPS) data indicated that the conversion of the stable radical pendant group to that of the oxoammonium cation was not due to the presence of a solvent. Specifically, the ATR-FTIR signature of the cation species (*i.e.*, +N=O) was distinct from that of the radical species (*i.e.*, N-O•), and this peak appeared at 1540 cm^{-1}, in good agreement with the small molecule salt analog (Figure 5a). Importantly, many peak assignments for the wavenumber associated with the N-O• bond stretch have been

made over a range of wavenumber values; however, none of the assignments appear at wavenumbers greater than 1500 cm^{-1}. This was consistent with the signal from the small molecule radical analog, TEMPO-OH (Figure 5a), as there was no peak present at wavenumbers from 1500-1600 cm^{-1}. Furthermore, the peak intensity at 1540 cm^{-1} increased for longer oxidation reaction times, prior to saturating in intensity, indicative of an increasing presence of a different chemical functionality. In addition to confirming the presence of the same three nitrogen environments observed in the FTIR-ATR spectra, XPS revealed also the presence of the balancing anion in $PTMA^+$ at binding energies of 220 eV and 270 eV for the Cl_{2p} and Cl_{2s} functionalities, respectively (data not shown). Comparison of the relative peak areas for the chlorine and nitrogen signals allowed for the quantification of the relative amounts of these two chemical entities. The entire nitrogen signal was used for the analysis because it remained constant for all PTMA samples, as the nitrogen atom does not participate in the oxidation reaction. Additionally, the nitrogen 1s peak exemplified three distinct nitrogen chemical states. Each peak was indicative of different chemical functionalities on the pendant groups of PTMA. The peak at the lower binding energy (BE) of 399.8 eV was assigned to the protected nitrogen (*i.e.*, N-H), and this is confirmed through acquisition of a similar XPS spectrum of the parent PTMPM polymer (data not shown). Moreover, the binding energies of the oxidized pendant groups were expected to be higher as they are known to increase as the oxidation state increased. Consequently, the signals associated with the N-O• and +N=O functionalities appeared at 401.3 eV and 405.6 eV, respectively. Similarly, by comparing the different chemical states of nitrogen, the +N=O concentration was found and compared well with the anion concentration, in agreement with charge neutrality. Utilizing XPS, the amount of $PTMA^+$ was quantified both by the presence of the +N=O cation on the macromolecular chains and the chlorine anion of the small molecule, confirming that the radical sites could be oxidized further to form the oxoammonium cationic species, and that this over-oxidation was coupled necessarily to the presence of the conjugate base of *m*CPBA.

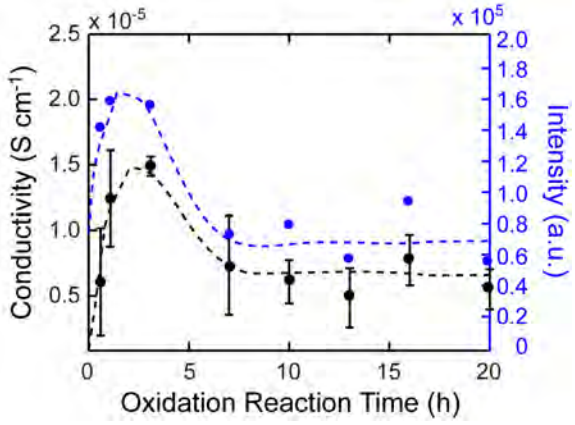

Figure 6. Electrical conductivity (left axis) as a function of oxidation time showing three regimes. Region 1 shows the functionalization of the pendant groups to the redox-active species occurring quickly for the first hour; thus the electrical conductivity increases. Region 2 highlights the window where mild intramolecular doping effects of the over-oxidized species (*i.e.,* $PTMA^+$) and the conductivity increases to a maximum average conductivity of 1.52 ± 0.3 × 10^{-5} S cm^{-1}. Region 3 includes the section where the effects of the protonation of the pendant groups in PTMA to N-OH significantly lower the electrical conductivity due to the insulation nature of these species. The intensity corresponding to the radical density as determined via EPR (right axis) as a function of oxidation time follows the electrical conductivity very well; therefore, as the radical density increases (*i.e.,* more charge transporting sites) the higher the electrical conductivity. The electrical conductivity was measured in devices of the geometry ITO/PTMA(200 nm)/Au. The symbols represent the average conductivity values and the error bars represent the standard deviation across 10 devices. The dashed lines serve as guides to the eye.

Critically, the presence of $PTMA^+$ sites affected the solid-state electrical conductivity of the radical polymer thin films in a drastic manner, and the maximum in electrical conductivity occurred at a doping level of ~2.5% cation sites. Furthermore, there were three regimes (Figure 6) that emerged in conductivity with respect to the oxidation reaction time to form PTMA from PTMPM. The first regime corresponded to shorter oxidation times where the polymer is being functionalized from the protected pendant group to the radical pendant groups. As such, as more pendant groups were available to participate actively in the charge transport mechanism the electrical conductivity increased. The second regime corresponded to intramolecular doping that occurred as the pendant groups are oxidized to $PTMA^+$. The effects of the electron poor pendant groups, $PTMA^+$, were very similar to the addition of electron-withdrawing dopants to π-conjugated polymers, which are known to increase the charge transport ability. Consequently, as the concentration of $PTMA^+$ increased the electrical conductivity triples to a value of $1.52 \pm 0.3 \times 10^{-5}$ S cm^{-1} at an oxidation time of 3 hours. Interestingly, the cation concentration stayed relatively constant after 3 hours, as shown by XPS and EPR. This indicated that this regime allowed for conversion of N-H functionalities to the stable radical functionality while a portion of the stable radicals were being converted to the oxoammonium cation as well. The last regime corresponded to long oxidation times where the electrical conductivity decreased significantly. The decrease in electrical conductivity was attributed to the protonation of the pendant groups. Once the pendant group reached this chemical state it could no longer participate in the oxidation-reduction reaction that transported charge, thus hindering the charge transport. As such, we attributed the decrease in electrical conductivity to the termination of redox active sites in PTMA for oxidation times exceeding 3 hours. Importantly, this effort was the first to correlate the molecular structure of radical polymer to the solid-state electrical conductivity of radical polymers. Additionally, it provided design rules towards the synthesis of radical polymers. We utilized these design rules in future experiments in order to quantify the mobility of PTMA as well.

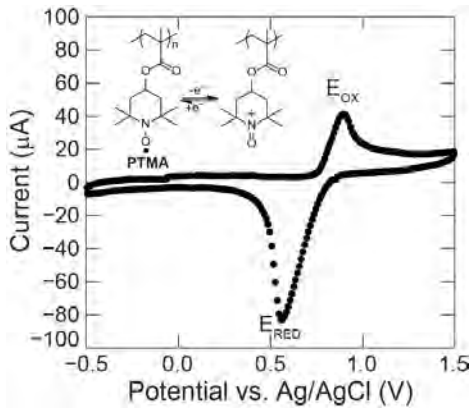

Figure 7. Cyclic voltammogram of a 25 mg of PTMA in 300 mL of dichloromethane (DCM) solution with 1 g of tetrabutylammonium tetrafluoroborate added to solution in order to serve as the supporting electrolyte. The scan was acquired at a rate of 100 mV s^{-1}. The reversible oxidation-reduction reaction for the PTMA species (left side of reaction arrow) that is occurring is displayed in the inset.

Specifically, we implemented a metal-semiconductor-metal (MSM) structure in order to apply the Mott-Gurney Law for the space charge-limited (SCL) model of charge transport. Under the assumptions that there was a sufficiently high voltage that the current density (J) resultant from both hole and electron diffusion was negligible, and that the carrier mobility (μ) was field-independent, the current density could be modeled by the following version of the Mott-Gurney equation.

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8L^3} \quad (1)$$

Here, ε_0 is the permittivity of free space, ε is the dielectric constant of the material, L is the thickness of the semiconducting layer, and V is the applied voltage. Importantly, the transport level of the PTMA was determined in order to establish that the contacts used in this study would result in the injection of only holes from the ITO contact. In a manner analogous to the Highest Occupied Molecular Orbital (HOMO) energy level discussed frequently in conjugated polymers, radical polymers have a Singularly Occupied Molecular Orbital (SOMO) energy level associated with the energy of the lone electron of the stable radical group present on the macromolecule. In order to verify the energy level of the SOMO relative to vacuum, cyclic voltammetry (CV) was utilized to establish the oxidation and reduction level of the PTMA in solution. The onset oxidation and reduction peaks versus an Ag/AgCl reference occurred at +0.8 V and +0.6 V, respectively (Figure 7). These values were then correlated to a solid-state energy level through the following well-known equation.

$$E_{HOMO} = -(1.2 \pm 0.1) \times q \times [V_{CV} + V_{REF}] \quad (2)$$

From these data, we calculated that the solid-state SOMO level of PTMA was 5.2 eV removed from vacuum. At a value of 5.2 eV removed from vacuum, this transport level allowed for the fabrication of hole-only devices if ITO was used as the bottom, injecting electrode and aluminum (Al) was used as the top collecting electrode, due to the work functions of the two materials (inset of Figure 8). Furthermore, due to the electrode asymmetry in the device, we have biased negatively the aluminum contact in order to provide an energetic barrier to charge injection from the top contact. By applying the Mott-Gurney analysis to the recorded current density-voltage (*J*-*V*) profiles of a device in this geometry, hole mobility values for the PTMA layer were calculated. As expected, a clear ohmic regime existed at low applied voltages. Then, as voltage was increased, a large region where the current density followed the square of the applied voltage (*i.e.*, the Mott-Gurney regime) was observed (0.8 V < *V* < 2.5 V for all devices, red line of Figure 8), and this was the space charge-limited regime. The dielectric constant of PTMA was measured to be ~3.4 using standard capacitance-voltage (C-V) measurements, in agreement with most polymeric systems. This allowed the hole mobility of PTMA to be determined through the use of Equation 1. Despite the complete lack of conjugation and crystallinity in the PTMA thin film, the measured hole mobility was ~10^{-4} cm^2 V^{-1} s^{-1}, which was on par with common semiconducting polymers [*e.g.*, poly(phenylene vinylene)s (PPVs) and poly(3-alkylthiophene)s (P3ATs)] when these materials were measured in space charge-limited current (SCL) devices. This key result added to the mounting evidence that the amorphous domains of semiconducting polymers can dominate charge transport in a large swath of

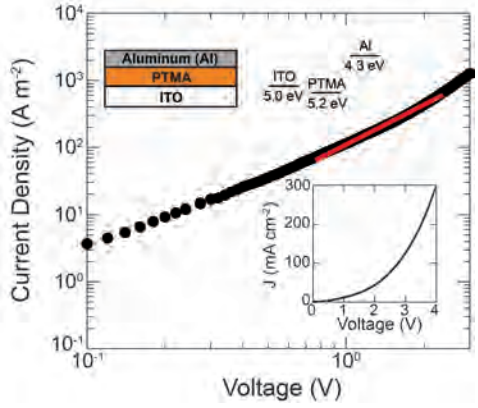

Figure 8. Current density as a function of applied voltage of a representative ITO/PTMA/Al device at room temperature. The red line depicts the region where J ~V^2. The inset in the bottom right is the same curve where the vertical axis has been plotted on a linear scale. The inset in the top left is the device structure and the associated charge transport energy level diagram. The device was tested such that the aluminum contact was biased with a negative voltage.

macromolecular systems due to the large number of grain boundaries that are present in macroscopic devices.

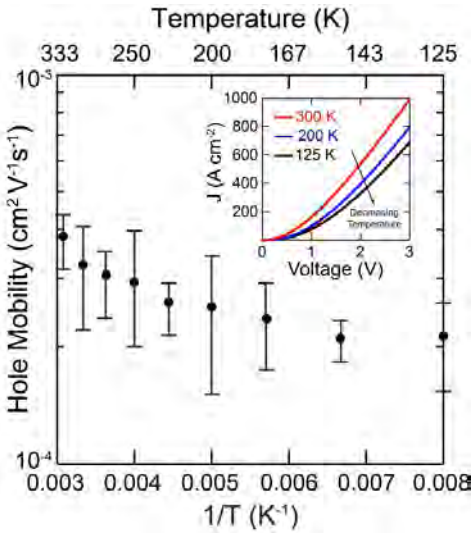

Figure 9. Temperature dependence of the hole mobility in an ITO/PTMA/Al fabricated device with a thickness of ~100 nm. The very slight temperature dependence is much less than what is expected for common conjugated polymer transport models, but is in good agreement with previous space charge-limited current results. Furthermore, this indicates that the density of radical sites and the ability of radical sites to interact is the rate-limiting step in the solid-state charge transport conduction mechanism of high glass transition temperature radical polymers. The data points shown are the average values and the error bars represent one standard deviation for a series of four different devices sampled at the indicated temperatures. The J-V curves for representative sweeps at representative temperatures are shown in the inset.

The mobility of holes in PTMA was a very weak function of temperature over normal operating temperature ranges, as shown in Figure 9. Importantly, these results indicated the nature of the rate-limiting step in the mechanism of charge hopping from radical site to radical site in radical-bearing polymers. While it would be expected that the redox reaction should be temperature dependent, this feature was not present in our solid-state system. This spoke to the relatively fast kinetics associated with the radical-to-cation and cation-to-radical transitions in these systems, and the relative quickness of this reaction was in good agreement with results for the PTMA redox reaction measured in solution. Therefore, it should not be surprising that charge could be transported at relatively high rates compared to classic conjugated polymer systems, assuming that the charge transfer sites were capable of interacting with one another in the solid state. However, the limiting step in charge transport must have been different in this system relative to semicrystalline polymer systems, as there were no crystalline domains in these amorphous polymers. Furthermore, in typical conjugated polymer systems, where charge transport between semicrystalline domains is the primary method of charge transport, an Arrhenius relationship would be expected between mobility and temperature. Because we did not observe this similar dependence, a temperature-independent model was established. In particular, the amorphous and isotropic nature of radical polymers dictated that charge transfer could only occur effectively if the two hopping sites were in close proximity. Therefore, if there was a great deal of molecular motion (resultant from the thermal energy available to the polymer bonds) there was a higher likelihood of the pendant groups coming into close contact. However, the glass transition temperature (T_g) of PTMA was known to be rather high (~170 °C) and approached the decomposition temperature. As such, it was difficult to access experimental temperatures where the PTMA side chains have a great deal of thermal motion while the polymer remains thermally-stable. In the temperature region examined here (125 K $\leq T \leq$ 333 K), the PTMA film was well into the glassy state and any change in temperature did not provide a great deal of additional rotational or translational energy to the polymer side chains in the solid state. Therefore, it was reasonable to

assert that the solid-state charge transport of this high glass transition radical polymer was limited by the relative proximity of an occupied radical site to an unoccupied radical site. Thus, if the density of radical sites could be increased or the relative interaction between neighboring pendant groups could be increased (*i.e.*, through a reduction in the glass transition temperature of the material away from the thermal decomposition temperature and closer to that of room temperature), we anticipate that the mobility would increase as well; this insight provides an excellent handle for the design of future generations of radical polymers.

After quantifying the conductivity and mobility of these radical polymers, we aimed to establish the environmental and bias stability of radical polymer thin films as well, as this has been an issue for certain conjugated polymer systems. Bias stressing of the PTMA thin films was performed and showed the inherent stability of PTMA when tested for 600 consecutive current-voltage sweeps. Devices were fabricated using two top electrodes (gold [Au] and silver [Ag]) that made an approximately ohmic contact with the singularly occupied molecular orbital (SOMO) transport level of PTMA at 5.2 eV, as evidenced by the linear response of the of the curves in Figure 10. Gold was chosen as the evaporated contact in order to prevent any effect from the oxidation of the metal contact when evaluating the performance of the PTMA. Specifically, current-voltage (I-V) sweeps from $-3\ \text{V} \leq V \leq 3\ \text{V}$ were consecutively applied for 600 sweeps, and, as can be seen in Figure 10a, the thin films showed consistent performance. These results illustrated two key remarks regarding the performance of these macromolecular thin films. First, the PTMA layer itself remained resistant to electrical breakdown during the course of the sweeping across voltage biases. The ability of the PTMA thin film to withstand the continuous sweeping at both negative and positive voltages demonstrated the resilience of the film from forming nanostructural defects. Additionally, the clear lack of hysteresis illustrated the robustness of the nitroxide radical within PTMA, showing that the charge transport redox mechanism was not hindered when electrical stressing occurs. Specifically, a decrease in electrical performance would have been expected had the radical sites recombined with other radical sites or were protonated (as seen with small molecule radicals when they are blended in a poly(methyl

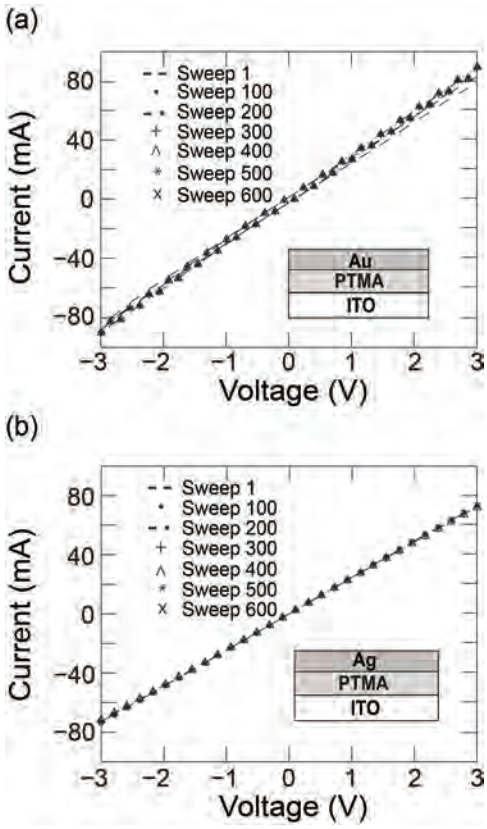

Figure 10. (a) Current vs. voltage plot illustrating the consecutive sweep stability of an ITO-PTMA-Au thin film. The graph depicts one representative device and each I-V curve corresponds to a specific sweep in the testing process. (b) Current vs. voltage plot depicting the stability of an ITO-PTMA-Ag thin film undergoing consecutive sweeping. Note that in both plots the curves representing different sweeps coincide well with one another, which causes the 7 curves to appear as 1 curve in each plot.

methacrylate) (PMMA) matrix) to form electrically-inactive pendant groups as they will no longer participate in the charge transport. While TEMPO radicals have been shown to obtain protons from neighboring radical sites at temperatures above 400 K to create a methyl-TEMPO, any resistive heating of the film during operation would not raise the local temperature to this large of a degree; therefore, the lack of this hysteresis was consistent with previous results for the small molecule nitroxide radical analog. In the limiting case that there were side reactions associated with the nitroxide sides, these effects were rather small. That is, any radical sites that were electrically destabilized or that were terminated did not inhibit current from flowing through the device. Thus, the electrical charges flowing through the film were not affected by the frequent change in electrical poling that occurs. In order to confirm that the consistent electrical performance was not due to contact effects between the gold top contact and PTMA layer, the same experiment was repeated using a silver top contact. Although there is a work function difference between gold and silver there is no significant difference in the electrical characterization of the PTMA device (*i.e.*, they both made ohmic contact), as shown in Figure 10b. Specifically, this indicated that the work function of the silver electrode was pinned by the SOMO level of PTMA at the organic-inorganic interface, and the films were of appropriate thickness such that interfacial defects caused by metal evaporation did not play a role in the transport through radical sites in the bulk of the film. Furthermore, the thin films evaluated using a silver top contact showed minimal differences in electrical performance when compared to those using gold as a top contact, as seen in the representative curves of Figure 10b. The slight decrease in electrical performance was attributed to variances in the film quality of the radical polymers during casting, and the difference in the magnitudes of the currents extracted at the given voltages for the gold and silver contacts were within the margin of error. Notably, the performance of PTMA upon electrical stressing of 600 consecutive sweeps demonstrated no degradation of the electrical performance indicative minimal loss of radical sites during the current-voltage cycles no matter the metal of contact used.

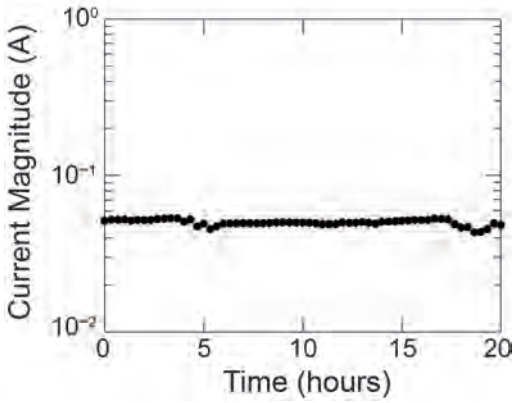

Figure 11. Plot with representative points illustrating a stable current magnitude over the course of 20 hours while being continuously biased at V = +2.0 V for an ITO-PTMA-Au thin film with a PTMA thickness of 400 nm. The small dips in the curve are due to sensitivities in the continuous measurement of current.

To further elucidate the effect of electrical stressing on the electrochemical stability of these macromolecular PTMA thin films over longer time periods, a constant positive or negative bias was applied to the ITO-PTMA-Au geometry devices. Here, the gold contact served as the grounded electrode. Specifically, the current was measured over the range of 20 hours during the biasing. These longer device operations were designed to elucidate if there was an effect on the chemistry of the radical sites in the PTMA and on the redox mechanism for charge transport. Furthermore, applying both a positive and negative bias elucidated whether the polarity of the electrode had an effect within the redox-active nature of the PTMA film or on the chemistry of the radical sites themselves. In this time period of being biased at +2.0 V, the PTMA films did not demonstrate degradation of the electrical performance (Figure 11). The

current remained at ~50 mA over the entire 20 hours. This behavior with a positive applied voltage confirmed that electrical biasing has no deleterious effects on the charge hopping redox reaction even after 20 hours of continuous operation. A similar study with exposure to a –2.0 V bias for the same time period (*i.e.*, 20 hours) was performed. The magnitude of current was the same as a positive applied bias, which was indicative of the efficacy and insensitivity of the redox reaction for charge transport to the direction of current flow within the radical polymer thin film. Vitally, the redox reaction prevailed after 20 hours of continuous operation and there was no effect on the transport due to the prolonged applied potential. These results were consistent with observations in radical polymer-based organic batteries, and were the first to translate these electrolyte-supported successes to the solid-state regime. Specifically, organic batteries showed very little degradation of radical sites within the polymer and showed little drop in overall device performance at applied biases for up to 500 sweep cycles. Along the same lines, and as seen in Figure 10, radical polymer thin films exhibit excellent electrochemical stability and reversibility of the redox reaction following extended operation times. The data of Figure 11 also confirmed that the radical sites in the polymer thin film remain stable over extended time frames regardless of bias poling. More specifically, the propensity for radical-radical reactions facilitated by electrical biasing was prevented by the bulky substituents neighboring the sites. Additionally, this design motif inhibited intramolecular hydrogen bonding from occurring within the polymer chains. As such, this provided increased evidence that radical polymers, and more specifically PTMA, could withstand the electrical stresses that are present in typical organic electronic devices.

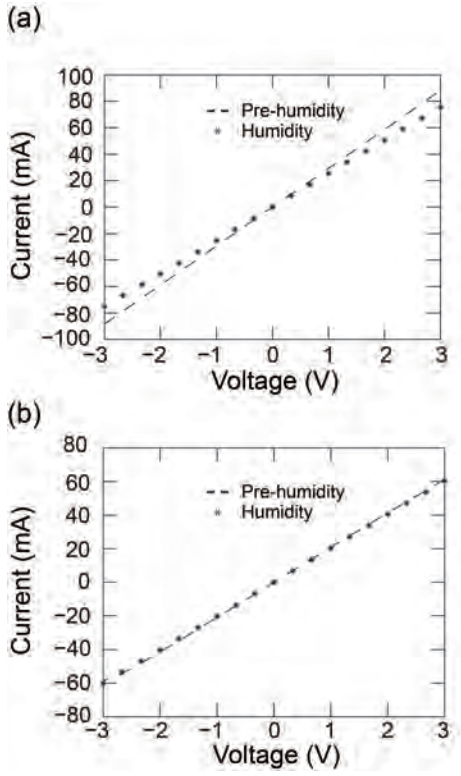

Figure 12. Thin films with the structure of ITO-PTMA-Au were fabricated and tested after exposure to different relative humidity (RH) values. (a) Thin films tested before and after 40% RH show minimal change in device performance. (b) Thin films exposed to 63% RH demonstrate an even smaller effect on the current after humidity exposure.

In addition, there was no observed effect on the electrochemical properties of the radical polymers upon the exposure of the radical polymer thin films to water vapor. Specifically, the capture and retention of water within the PTMA thin films could result in the protonation of the radical pendant moieties, as has been previously observed. Furthermore, the protonation of radical sites upon exposure to humidity could have generated inactive pendant groups that would not participate in the charge transport and, in turn, significantly hindered the applicability of these materials in wide-scale organic electronic applications. Here, the propensity of nitroxide radicals to react with water molecules to create inactive sites for charge transport in radical polymers was examined. Specifically, PTMA thin films were tested in vacuum. Next, the thin

films were exposed to a range of relative humidity (RH) values for 2 hours prior to retesting in vacuum. For the 40% RH value, there was an 8% reduction in the current (at a given applied voltage) after the radical polymer film as exposed to humidity (Figure 12a). However, this did not significantly affect the overall electrical conductivity of the PTMA. Moreover, the films exposed to a higher RH value of 63% exhibited smaller decreases in their current vs. voltage behaviors (Figure 12b). The consistent electrical performances of the functional thin films pre- and post-exposure to varying levels of relative humidity were a testament to the radical sites insensitivity to water vapor. Lastly, the thin films were exposed to an RH of 80% for 2 hours, and there was minimal change in electrical performance before and after exposure to the water vapor. In addition, the devices exposed to 80% RH were also swept 600 times consecutively and the electrical properties of the thin films remain relatively unchanged. The stability of the nitroxide radical in the presence of water was key in the development of new and more efficient radical polymers for electronic applications. We note that, although, radical molecules have demonstrated the propensity to serve as proton scavengers, they often require high-energy environments for the reactions to occur, usually elevated temperatures. As such, it was reassuring that at room temperature the nitroxide radical in PTMA thin films remained stable after exposure to humid environments and a range of continuous electrical testing.

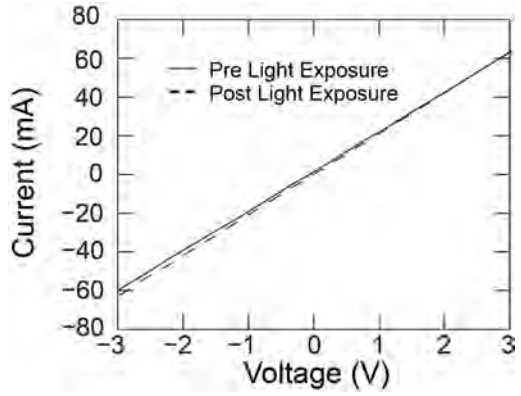

Figure 13. Current-voltage behavior of an ITO-PTMA-Au thin film before and after light exposure for 2 hours from an AM 1.5 solar simulator. The nearly identical behavior before and after light exposure indicate that short term light degradation does not inhibit charge transport within the PTMA film.

Moreover, PTMA thin films were irradiated with solar light and the effects on the electrical properties were monitored. Specifically, while the use of PTMA as an anodic interfacial modifier in inverted geometry OPV devices has been demonstrated, the effect that sustained illumination exposure has on the PTMA layer itself was not evaluated. For example, light irradiation can catalyze the oxidation between oxygen and the conjugated thiophene ring on the backbone of poly(3-hexylthiophene). As a result, the conjugation is broken and the electronic properties suffer. As such, the effect of solar light in combination with ambient conditions (RH ~40%) was monitored on thin film PTMA devices. After thin film ITO-PTMA-Au devices were fabricated, they were tested in vacuum under similar conditions as above, with a bias range of $-3\ \text{V} \leq V \leq 3\ \text{V}$ (Figure 13). Next, the PTMA thin films were exposed to solar radiation through the transparent ITO contact for two hours under ambient conditions. In this manner, the light could serve as the catalyst to facilitate the proton scavenging observed with radical containing small molecules. As seen in Figure 13, the magnitude of the current at a given voltage (across the entire voltage range examined) remained nearly identical before and after light exposure. This indicated that there is no photo-induced protonation of the radical sites in these shorter time periods, and further confirmed the robustness of the radical sites themselves. This may be a rather expected result as the thin films of PTMA are very weakly absorbing, and it seems apparent from these results that the irradiation was not sufficient to catalyst the radicals to serve as proton scavengers. Additionally, no film cracking or surface defects occurred during and after

light exposure. Because the nitroxide radical has the ability to withstand degradation under short periods of focused illumination, nitroxide radical based radical polymers such as PTMA remain viable candidates for study in more advanced organic electronic systems.

While these experiments established the viability of PTMA, a clear advantage of radical polymers over conjugated macromolecules is the synthetic flexibility of the materials. To demonstrate this fact, we synthesized and characterized the nanostructure of radical-containing diblock copolymers. This is because the implementation of semiconducting and conducting moieties in block polymer materials is an increasingly-studied field because controlling the nanostructure of many organic electronic devices is of prime import. However, the use of π-conjugated semiconducting and conducting moieties in block polymer systems usually leads to more complicated microphase separation behavior than that associated with non-conjugated systems. These additional complexities include the fact that the rigid macromolecular backbone of conjugated polymer systems impacts the number of chain conformations available to the block polymer system. Furthermore, in many instances, the conjugated polymer moiety is semicrystalline at room temperature. Therefore, microphase separation between the moieties of the block polymer system due to chemical dissimilarity and the entropy of chain stretching can be dominated by crystallization of the conjugated block. This can be overcome through careful design of the thermal transitions of the semicrystalline moiety of the block polymer, but it often leads to block polymer systems that rarely self-assemble into the more oft-observed coil-coil nanostructures (*e.g.*, hexagonally-packed cylinders, gyroid structures) that are advantageous for a number of organic electronic applications. As such, the ability to utilize radical polymers with non-conjugated macromolecular backbones provides the important dual effect of: 1) reducing the complexity of thin film self-assembly while 2) simultaneously providing a block polymer where at least one moiety is electronically-active.

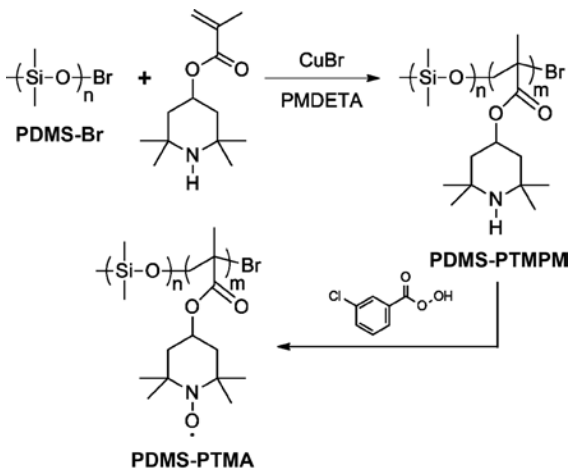

Figure 14. The ATRP-mediated route employed for the synthesis of PDMS-PTMA using PDMS-Br as the macroinitiator, PMDETA as the ATRP ligand, CuBr as the ATRP catalyst, and TMPM as the monomer for the second block. The resulting PDMS-PTMPM was oxidized with *m*CPBA to form the radical copolymer PDMS-PTMA.

Specifically, we implemented atom transfer radical polymerization (ATRP) in order to readily synthesize well-defined ($Đ \leq$ 1.25) polydimethylsiloxane-*b*-poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PDMS-PTMA) diblock polymers using a PDMS-based macroinitiator. Furthermore, the thin film nanostructural ordering of diblock copolymers was evaluated systematically across a range of diblock copolymer compositions and molecular weights. Specifically, through proper solvent annealing of the PDMS-PTMA thin films, we established that a number of microphase separated structures of the diblock copolymer can be observed. This control of the self-assembly of electronically-active, radical polymer-based diblock copolymers presents itself as an exciting opening for the rationale design and control of nanostructured organic electronic materials. In

this work, the first block (*i.e.*, PDMS-Br) of known molecular weight was utilized as the macroinitiator from which the PTMPM block was grown (Figure 14). Here PDMS was used as the insulating moiety due to the high chain mobility of PDMS at and above room temperature. This helped to facilitate the nanostructural ordering observed in the diblock copolymer thin film samples upon solvent annealing (*vide infra*). Following two purification steps, the PDMS-PTMPM diblock copolymers were analyzed using ^{1}H NMR to determine their purity as well as the molecular weight of the PTMPM moieties. Because of the controlled nature associated with the ATRP mechanism, the molecular weight of the PTMPM segment could be tuned in a rather straightforward manner (*i.e.*, through control of the relative ratios of the polymerization reagents) and, the molecular weights of the PTMPM blocks were determined readily through integration of the proton resonances associated with the methyl protons on the silicon of the PMDS-Br backbone and the proton on the PTMPM pendant ring In particular, the ATRP scheme employed was capable of synthesizing PTMA moieties with molecular weight values that ranged from 10 kg mol^{-1} to 71 kg mol^{-1} in a straightforward fashion. Next, utilizing a previously established method, the parent polymers (*i.e.*, PDMS-PTMPM) were converted to the radical-bearing functionality using *m*CPBA as the oxidizing agent to produce the PDMS-PTMA diblock copolymers. We note that the oxidation procedure did not affect the PDMS block of the diblock copolymer, as was the case in previous reports where polystyrene (PS) was utilized as the second block of a PTMA-based diblock copolymer. The SEC traces of the PDMS-PTMA samples demonstrated a clear shift in elution time corresponding well to the increasing molecular size in the diblock system (Figure 15b). Additionally, the dispersity values of all the PDMS-PTMA samples synthesized remained relatively low (*i.e.*, $Đ < 1.25$), confirming that the polymerization occurred in a controlled manner. We do note that, for the higher molecular weight PTMA blocks [*e.g.*, PDMS(10)-PTMA(36) and PDMS(10)-PTMA(71)], a slight shoulder at lower elution volumes was observed; however the dispersity values of these samples also remained at values of $Đ \leq 1.25$.

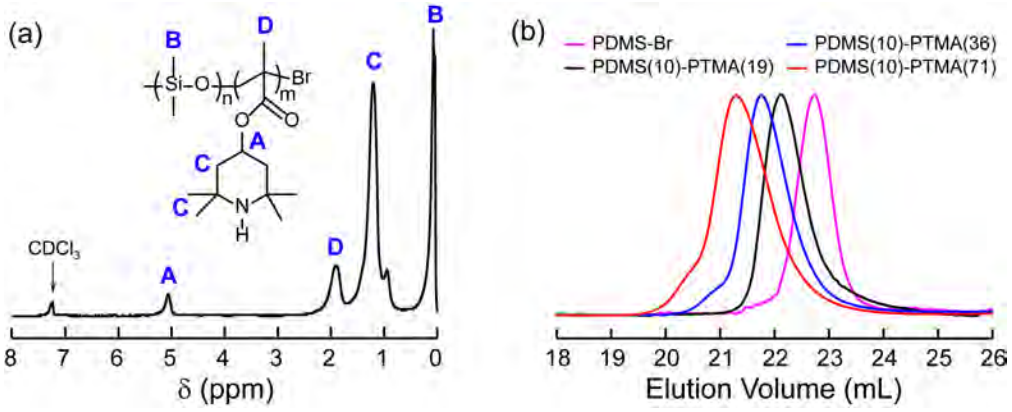

Figure 15. (a) A representative ^{1}H NMR spectrum for the purified PDMS(10)-PTMPM(10) diblock copolymer dissolved in deuterated chloroform ($CDCl_3$). The integration of the peaks associated with the resonances labeled **A** and **B** allowed for the number-average molecular weight of the PTMPM moiety to be determined in a straightforward manner. (b) SEC traces for the PDMS-Br homopolymer and representative PDMS-PTMA diblock copolymers over the entire range of the diblock copolymers synthesized. All SEC experiments were performed with a mobile phase of THF flowing at a rate of 1 mL min^{-1} and at temperature of 35 °C.

The specific presence of the radical moieties pendant to each of the repeat units were monitored through electron paramagnetic resonance (EPR) spectroscopy, as has been shown

previously for numerous electronically-active radical polymer systems. The absorption of the nitroxide radical is well established and occurred at a magnetic field of 3358 G, which corresponded very well with the PDMS-PTMA absorption (Figure 16). In order to quantify the degree to which the PTMPM moiety was converted to the PTMA moiety (*i.e.*, the fraction of repeat units on the PTMA chain that contained a stable radical group) the EPR absorption spectra were normalized to the small molecule TEMPO-OH absorption spectrum. This was because the TEMPO-OH signal was similar to the nitroxide functionality associated with PTMA, and it was known that each TEMPO-OH molecule contains a single radical site. In this way, a direct comparison could be made. All of the samples showed a reasonable (*i.e.*, $\geq$ 34%) fraction of radical groups. Furthermore, the fraction of radical groups present was relatively consistent between the PDMS-PTMA diblock copolymers. As such, we were confident that the chemical dissimilarities between the two segments of the PDMS-PTMA diblock copolymers that self-assemble (described below) were, to first order, the same.

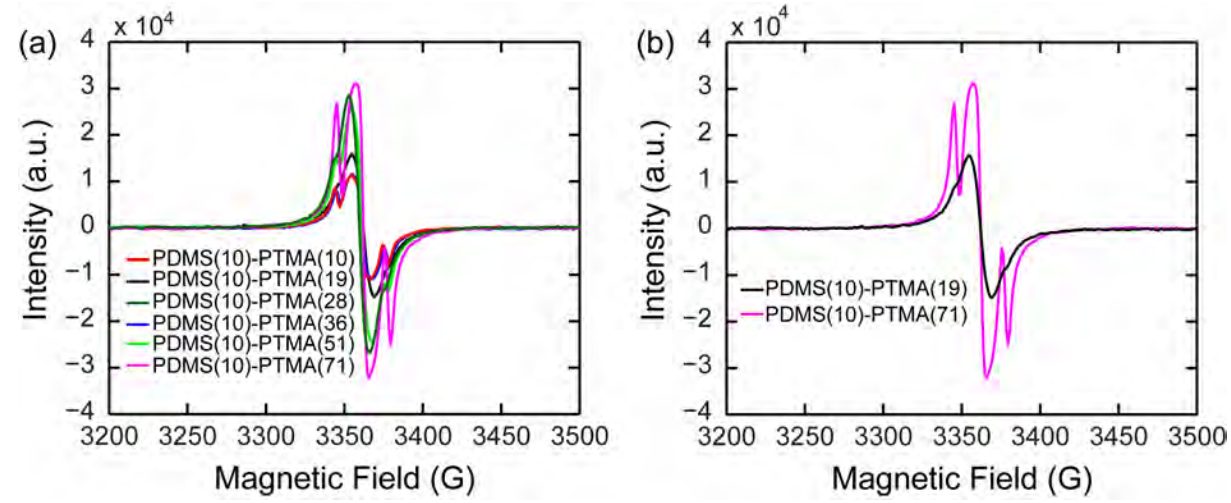

Figure 16. (a) EPR spectra of a range of PDMS-PTMA diblock copolymers in toluene at a concentration of 2 mg mL^{-1}. These data demonstrate the higher absorption (*i.e.*, higher radical density) for PTMA moieties with weight fractions of PTMA present in the PDMS-PTMA diblock copolymers. Additionally, the PDMS-PTMA diblock copolymers with larger molecular weights of PTMA demonstrate hyperfine splitting, suggesting less radical-to-radical interactions. As an example of this, (b) isolates the EPR spectra for PDMS(10)-PTMA(71) and PDMS(10)-PTMA(19) and PMDS(10)-PTMA(71).

Interestingly, as the molecular weight of the PTMA block increased beyond 20 kg mol^{-1} (*i.e.*, $w_{PTMA} \geq 0.70$), it was evident that splitting of the absorption peaks occurs (Figure 16a). This phenomenon (*i.e.*, hyperfine splitting) was indicative of reduced radical-to-radical interactions in the EPR solution (Figure 16b). Importantly, the hyperfine splitting suggested that, as the size of the PTMA block increased, the polymer chains adopt a different conformation in solution. In this conformation, the radical sites were necessarily farther removed in space despite the fact that a larger percentage of the diblock copolymer contained radical sites.

While the solution-state behavior of PDMS-PTMA was notable and worthy of further study, in order to be of high utility in organic electronic applications (*e.g.*, solid-state batteries), the ability of these PDMS-PTMA materials to generate well-defined nanostructures as thin films was of primary concern. While this has been an important point of research for

optoelectronically-active block polymers based on π-conjugated macromolecules, only a few select efforts have been able to show distinct assembly of these materials that is unique from what is observed due to the crystallization of the homopolymer conjugated polymer. By utilizing non-conjugated, amorphous radical polymers as the electronically-active moiety of the block copolymer, our work circumvented this common roadblock. As expected for coil-coil diblock copolymer thin films, nanoscale features were observed over a large range of polymer molecular weights when the PDMS-PTMA thin films were cast as thin films. Due to the rather high glass transition temperature of PTMA and the unstable thermal nature of the radical group associated with the nitroxide group (*i.e.*, degradation of the polymer beings to occur at T ~210 °C), thermal annealing of these materials was very difficult. Instead, solvent annealing in chloroform vapor was implemented to provide mobility to both the PDMS and PTMA moieties of the diblock copolymer. For diblock copolymers containing a higher weight fraction of the relatively mobile PDMS moiety, the exposure to chloroform vapors led to relatively well-defined, nanostructured PDMS-PTMA thin films with either lamellar (Figure 17a) or cylindrical (Figure 17b) morphologies, as imaged with atomic force microscopy (AFM). The domain sizes observed were on the order of 30 – 40 nm for all samples that showed clear nanostructural ordering (*i.e.*, those with higher PDMS content). However, as the weight fraction of the PTMA block was increased, the ability to form ordered thin film nanostructures is decreased through the use of solvent annealing (Figure 17c). This was associated with the limited mobility of the PTMA block, and it could attributed to its high glass transition (*i.e.*, >150 °C). This high thermal transition is well-known in PTMA, and it occurs due to the relatively bulky and polar 2,2,6,6-tetramethylpiperidinyloxy-4-yl side chain of the macromolecule.

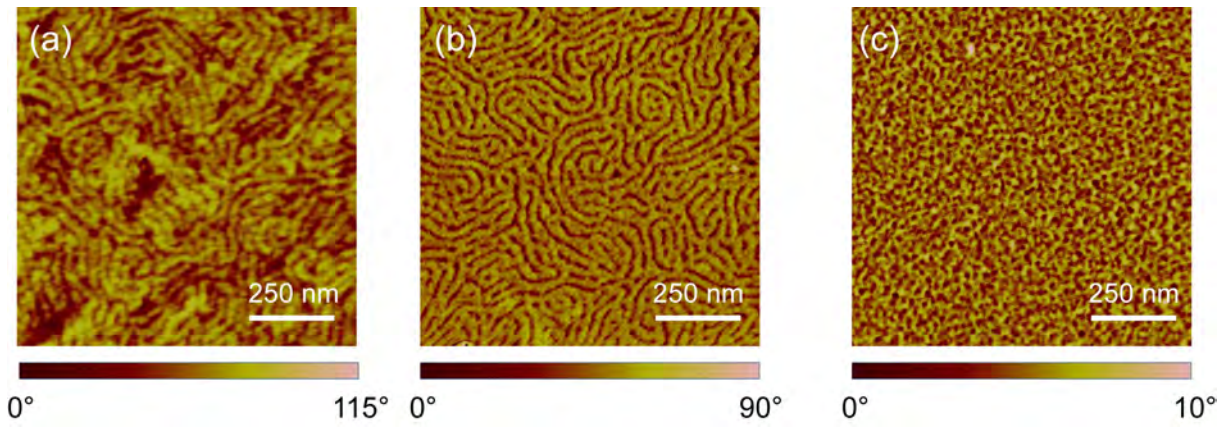

Figure 17. AFM phase images of (a) PDMS(10)-PTMA(10), (b) PDMS(10)-PTMA(36), and (c) PDMS(10)-PTMA(51) thin films after annealing with chloroform vapors for 24 h at room temperature. The PDMS(10)-PTMA(10) thin film showed a lamellar morphology while the PDMS(10)-PTMA(36) system showed a cylindrical microstructure. Samples with large weight fractions of PTMA did not order in the thin film after exposure to the solvent annealing procedure.

Conclusions

During the performance of this grant, three key objectives have been reached. We have been able to: (1) demonstrate the robustness associated with the synthesis of radical polymers; (2) highlight the care that must be taken when generating radical polymers such that there electronic performance can be optimized; and (3) demonstrate that radical polymers have very,

very promising charge transport characteristics in the solid-state. The conclusions that are readily drawn from these results are that radical polymers are emerging solid-state conducting materials. Therefore, they could be of significant interest in nearly any flexible electronics system. Clearly, future avenues of work need to target strategies that will increase the charge transport ability of the radical polymers. However, the design rules that we have outlined in this report (and the publications that are resultant from this project) outline a clear path towards this future success. As such, this project has allowed for us to significantly advance the state-of-the-art in organic electronics, and it has allowed us to establish our laboratory as a world-leader in the field. For these two facts, we sincerely thank the AFOSR, Dr. Charles Lee, and the Young Investigator Program.

1.

1. Report Type

Final Report

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Organization / Institution name

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Grant/Contract Title

The full title of the funded effort.

Molecular Design and Device Application of Radical Polymers for Improved Charge Extraction in Organic Photovoltaic Cells

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-12-1-0243

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Bryan W. Boudouris

Program Manager

The AFOSR Program Manager currently assigned to the award

Dr. Charles Lee

Reporting Period Start Date

05/01/2012

Reporting Period End Date

04/30/2015

Abstract

Radical polymers (i.e., macromolecules composed of non-conjugated backbone architectures and with stable radical sites present on the pendant groups of these backbones) are emerging as promising materials for organic electronic applications. While these materials have been used in a limited number of electrolyte-supported energy conversion and storage applications, the work presented within summarizes the first systematic findings of structure-property-performance relationships with respect to the solid-state electrical conductivity of radical polymers. In particular, we established the ready, scalable, and controlled synthesis of open-shell macromolecular homopolymers and block polymers. Furthermore, the solid-state electrical conductivity of a model radical polymer was determined to be of ~10-5 S cm-1. This is on the same order of magnitude as common pristine (i.e., not doped) π-conjugated polymers, which highlights the great promise of these next-generation materials. Additionally, the environmental stability (i.e., resistance to oxygen and humidity) and voltage-dependence of radical polymer thin films was found to be quite robust; this was despite the lone electron nature of the radical site. Therefore, these radical polymers have proven to be: (1) synthetically-simple, (2) environmentally-robust, and (3) relatively high-performing with respect to many oft-used conjugated polymers. Because of these advantageous properties, radical polymer thin films have been included in a number of advanced organic electronic devices. Thus, through the support of the

AFOSR and the Young Investigator Program, we have been able to establish these macromolecules as exciting alternatives to traditional polymer conductors. Moreover, this effort has established our laboratory as a world leader in the polymer synthesis, polymer physics, and solid-state device application of these unique macromolecules. As such, this program has advanced the state-of-the-art with respect to novel polymer electronics and promoted the career of an early-stage investigator with a research portfolio centered on the needs of the Department of Defense.

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Archival Publications (published) during reporting period:

Seven manuscripts have been published to date due to work supported by the AFOSR YIP award. Furthermore, 1 manuscript is currently in press, 2 manuscripts are under review currently, and 1 manuscript is in preparation. Therefore, we anticipate having, at least, a final total of 11 manuscripts published due to the support of the AFOSR YIP award (see below for exact referencing). We note that all publications have recognized the support of the AFOSR in the Acknowledgements sections of the manuscripts.

The seven published manuscripts are the following.

1. “Engineering Optoelectronically-active Macromolecules for Polymer-based Photovoltaic and Thermoelectric Devices,” Boudouris, B. W. Current Opinion in Chemical Engineering 2013, 2, 294-301.

2. “Controlled Radical Polymerization and Quantification of Solid State Electrical Conductivities of Macromolecules Bearing Pendant Stable Radical Groups,” Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. ACS Applied Materials and Interfaces 2013, 5, 9896-9901.

3. “Quantification of Solid-State Charge Mobility in a Model Radical Polymer,” Baradwaj, A. G.; Rostro, L.; Alam, M. A.; Boudouris, B. W. Applied Physics Letters 2014, 104, 213306.

4. “Solid State Electrical Conductivity of Radical Polymers as a Function of Pendant Group Oxidation State,” Rostro, L.; Wong, S. H.; Boudouris, B. W. Macromolecules 2014, 47, 3713-3719.

5. “Defect Characterization in Organic Semiconductors: Forward Bias Capacitance Analysis,” Ray, B.; Baradwaj, A. G.; Boudouris, B. W.; Alam, M. A. Journal of Physical Chemistry C 2014, 118, 17461–17466.

6. “Radical-containing Polymers and Their Applications to Organic Electronic Devices,” Tomlinson, E. P.; Hay, M. E.; Boudouris, B. W. Macromolecules 2014, 47, 6145–6158.

7. “Synthesis and Thin Film Self-Assembly of Radical-Containing Diblock Copolymers,” Rostro, L.; Baradwaj, A. G.; Muller, A. R.; Laster, J. L.; Boudouris, B. W. MRS Communications 2015, available online.

The one manuscript that has been accepted is the following.

8. “Collection-limited Theory Interprets the Extra-ordinary Response of Single Semiconductor Organic Solar Cells,” Ray, B.; Baradwaj, A. G.; Khan, M. R.; Boudouris, B. W.; Alam, M. A. Proceedings of the National Academy of Science 2015, accepted.

The two manuscripts that are under review are the following.

9. “Design of Super-Paramagnetic Core-Shell Nanoparticles for Enhanced Performance of Inverted Polymer Solar Cells,” Jaramillo, J.; Barrero, C.; Boudouris, B. W.; Jaramillo, F. 2015, submitted for review.

10. “On the Environmental and Electrical Bias Stability of Solid-State Radical Polymer Conductors,” Baradwaj, A. G.; Rostro, L.; Boudouris, B. W. 2015, submitted for review.

The one manuscript that is in preparation is the following.

11. “Enhanced Electrical Conductivity in Radical Polymers through Systematic Doping with Small Molecule Salts,” Baradwaj, A. G.; Jochem, K. S.; Boudouris, B. W. 2015, in preparation.

Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

Extensions granted or milestones slipped, if any:

None

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
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Equipment/Facilities			
Supplies			
Total			

Report Document

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Appendix Documents

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